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Date: September 28, 2000

In Re Application of:

Martin TOPSOE, Asa WENDSJO, Steen YDE-ANDERSEN

Serial No: To be assigned
(U.S. National Phase of
International Application No. PCT/EP99/02102
Filed March 29, 1999

Filed: Concurrently herewith

For: METHOD OF MAKING POLYMER ELECTROLYTE
ELECTROCHEMICAL CELLS

AFFIRMATION OF PRIORITY CLAIM

Hon. Commissioner of
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Box PCT
Washington, DC 20231
Attn: DO/EO/US

Sir:

Priority has been claimed on the basis of Great Britain Patent Application No. 9806831.5 filed March 30, 1998. A certified copy of Great Britain Patent Application No. 9806831.5 was received by the International Bureau on May 25, 1999, during the pendency of International Application No. PCT/EP99/02102. Applicants herewith affirm the priority claim of the aforesaid Great Britain patent application.

1990 1991 1992 1993 1994 1995 1996 1997 1998 1999 2000 2001 2002 2003 2004 2005 2006 2007 2008 2009 2010 2011 2012 2013 2014 2015 2016 2017 2018 2019 2020 2021 2022 2023 2024 2025 2026 2027 2028 2029 2030 2031 2032 2033 2034 2035 2036 2037 2038 2039 2040 2041 2042 2043 2044 2045 2046 2047 2048 2049 2050 2051 2052 2053 2054 2055 2056 2057 2058 2059 2060 2061 2062 2063 2064 2065 2066 2067 2068 2069 2070 2071 2072 2073 2074 2075 2076 2077 2078 2079 2080 2081 2082 2083 2084 2085 2086 2087 2088 2089 2090 2091 2092 2093 2094 2095 2096 2097 2098 2099 2100 2101 2102 2103 2104 2105 2106 2107 2108 2109 2110 2111 2112 2113 2114 2115 2116 2117 2118 2119 2120 2121 2122 2123 2124 2125 2126 2127 2128 2129 2130 2131 2132 2133 2134 2135 2136 2137 2138 2139 2140 2141 2142 2143 2144 2145 2146 2147 2148 2149 2150 2151 2152 2153 2154 2155 2156 2157 2158 2159 2160 2161 2162 2163 2164 2165 2166 2167 2168 2169 2170 2171 2172 2173 2174 2175 2176 2177 2178 2179 2180 2181 2182 2183 2184 2185 2186 2187 2188 2189 2190 2191 2192 2193 2194 2195 2196 2197 2198 2199 2200 2201 2202 2203 2204 2205 2206 2207 2208 2209 2210 2211 2212 2213 2214 2215 2216 2217 2218 2219 2220 2221 2222 2223 2224 2225 2226 2227 2228 2229 2230 2231 2232 2233 2234 2235 2236 2237 2238 2239 2240 2241 2242 2243 2244 2245 2246 2247 2248 2249 2250 2251 2252 2253 2254 2255 2256 2257 2258 2259 2260 2261 2262 2263 2264 2265 2266 2267 2268 2269 2270 2271 2272 2273 2274 2275 2276 2277 2278 2279 2280 2281 2282 2283 2284 2285 2286 2287 2288 2289 2290 2291 2292 2293 2294 2295 2296 2297 2298 2299 2300 2301 2302 2303 2304 2305 2306 2307 2308 2309 2310 2311 2312 2313 2314 2315 2316 2317 2318 2319 2320 2321 2322 2323 2324 2325 2326 2327 2328 2329 2330 2331 2332 2333 2334 2335 2336 2337 2338 2339 2340 2341 2342 2343 2344 2345 2346 2347 2348 2349 2350 2351 2352 2353 2354 2355 2356 2357 2358 2359 2360 2361 2362 2363 2364 2365 2366 2367 2368 2369 2370 2371 2372 2373 2374 2375 2376 2377 2378 2379 2380 2381 2382 2383 2384 2385 2386 2387 2388 2389 2390 2391 2392 2393 2394 2395 2396 2397 2398 2399 2400 2401 2402 2403 2404 2405 2406 2407 2408 2409 2410 2411 2412 2413 2414 2415 2416 2417 2418 2419 2420 2421 2422 2423 2424 2425 2426 2427 2428 2429 2430 2431 2432 2433 2434 2435 2436 2437 2438 2439 2440 2441 2442 2443 2444 2445 2446 2447 2448 2449 2450 2451 2452 2453 2454 2455 2456 2457 2458 2459 2460 2461 2462 2463 2464 2465 2466 2467 2468 2469 2470 2471 2472 2473 2474 2475 2476 2477 2478 2479 2480 2481 2482 2483 2484 2485 2486 2487 2488 2489 2490 2491 2492 2493 2494 2495 2496 2497 2498 2499 2500 2501 2502 2503 2504 2505 2506 2507 2508 2509 2510 2511 2512 2513 2514 2515 2516 2517 2518 2519 2520 2521 2522 2523 2524 2525 2526 2527 2528 2529 2530 2531 2532 2533 2534 2535 2536 2537 2538 2539 2540 2541 2542 2543 2544 2545 2546 2547 2548 2549 2550 2551 2552 2553 2554 2555 2556 2557 2558 2559 2560 2561 2562 2563 2564 2565 2566 2567 2568 2569 2570 2571 2572 2573 2574 2575 2576 2577 2578 2579 2580 2581 2582 2583 2584 2585 2586 2587 2588 2589 2590 2591 2592 2593 2594 2595 2596 2597 2598 2599 2600 2601 2602 2603 2604 2605 2606 2607 2608 2609 2610 2611 2612 2613 2614 2615 2616 2617 2618 2619 2620 2621 2622 2623 2624 2625 2626 2627 2628 2629 2630 2631 2632 2633 2634 2635 2636 2637 2638 2639 2640 2641 2642 2643 2644 2645 2646 2647 2648 2649 2650 2651 2652 2653 2654 2655 2656 2657 2658 2659 2660 2661 2662 2663 2664 2665 2666 2667 2668 2669 2670 2671 2672 2673 2674 2675 2676 2677 2678 2679 2680 2681 2682 2683 2684 2685 2686 2687 2688 2689 2690 2691 2692 2693 2694 2695 2696 2697 2698 2699 2700 2701 2702 2703 2704 2705 2706 2707 2708 2709 2710 2711 2712 2713 2714 2715 2716 2717 2718 2719 2720 2721 2722 2723 2724 2725 2726 2727 2728 2729 2730 2731 2732 2733 2734 2735 2736 2737 2738 2739 2740 2741 2742 2743 2744 2745 2746 2747 2748 2749 2750 2751 2752 2753 2754 2755 2756 2757 2758 2759 2760 2761 2762 2763 2764 2765 2766 2767 2768 2769 2770 2771 2772 2773 2774 2775 2776 2777 2778 2779 2780 2781 2782 2783 2784 2785 2786 2787 2788 2789 2790 2791 2792 2793 2794 2795 2796 2797 2798 2799 2800 2801 2802 2803 2804 2805 2806 2807 2808

As a result of the above, the following are the main findings of the study:

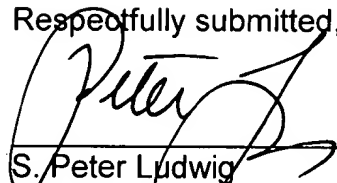
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Page 2

Dated: September 28, 2000

Respectfully submitted,



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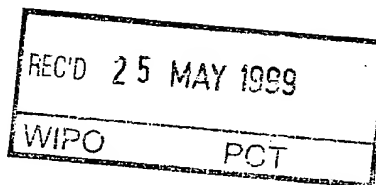
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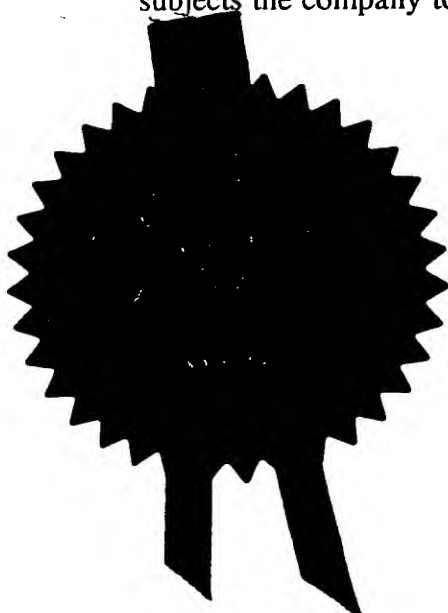
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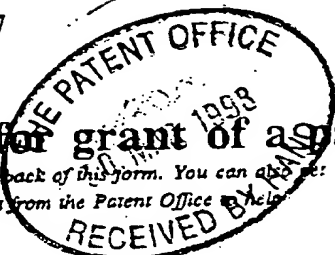
31MAR98 E349717-1 013295
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Cardiff Road
Newport
Gwent NP9 1RH



1. Your reference

JIM/LJ/PO2055

2. Patent application number

(The Patent Office will fill in this part)

30 MAR 1998

9806831.5

3. Full name, address and postcode of the or of
each applicant (underline all surnames)

DANIONICS A/S
HESTEHAVEN 21J
DK-5260 ODENSE S
DENMARK

Patents ADP number (if you know it)

If the applicant is a corporate body, give the
country/state of its incorporation

DENMARK

07405107001

4. Title of the invention

POLYMER ELECTROLYTE ELECTROCHEMICAL CELL

5. Name of your agent (if you have one)

ELKINGTON AND FIFE

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to which all correspondence should be sent
(including the postcode)

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Patents ADP number (if you know it)

67004

6. If you are declaring priority from one or more
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and the date of filing of the or each of these
earlier applications and (if you know it) the or
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Priority application number
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Date of Filing
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derived from an earlier UK application,
give the number and the filing date of
the earlier application

Number of earlier application

Date of Filing
(day/month/year)

Patents Form 1/77

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer "Yes" if:
- YES
- a) any applicant named in part 3 is not an inventor, or
b) there is an inventor who is not named as an applicant, or
c) any named applicant is a corporate body.

See note (d))

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Continuation sheets of this form:	NONE
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Claim(s)	6
Abstract	1
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Priority documents	-
Translations of priority documents	-
Statement of inventorship and right to grant of a patent (Patents Form 7/77)	4
Request for preliminary examination and search (Patents Form 9/77)	-
Request for substantive examination (Patents Form 10/77)	-
Any other documents (please specify)	-

11. I/We request the grant of a patent on the basis of this application.

Signature



Date

30/03/1998

12. Name and daytime telephone number of person to contact in the United Kingdom

Mr J I MARCHANT
01732 458881

Polymer Electrolyte Electrochemical C 11

5 The recent development of electrochemical cells based on lithium containing negative electrode structures has allowed the fabrication of cells of high energy density. Cells have been obtained, which display energy densities beyond 200 Wh/l and even 250 Wh/l has been reported.

10 In order to reach such high energy densities, the capacity utilisation of the active materials in the cell should be high. As further high rate capabilities of the electrochemical cells are sought, electrolyte phases should provide low impedance.

15 Traditionally, high conductivity electrolytes have been liquid electrolytes. Such electrolytes are used in lithium cells of intercalation compound electrodes; The positive electrode structures are based on transition metal oxides operating at a potential close to 4V vs. Li/Li⁺. Negative
20 electrode structures of carbons and graphites may be applied, which reversibly intercalate lithium at a potential close to the potential of metallic lithium. Such cells are referred to as lithium-ion cells, as the active lithium is always in its ionic form. Alternatively,
25 negative electrode structures of alloys such as Li-Al and Li-Sn may be used. Such cells will be referred to as lithium-alloy cells. All of the above configurations provide voltages close to 4V.

30 As high energy density and high rate capability imply reduced safety, an important objective in the development of such electrochemical cells has been to improve the safety aspects of the use of such cells.

The main improvement in terms of safety has been the substitution of carbon or alloy structures for the pure lithium metal negative electrode structures. During operation of lithium metal based negative electrodes, dendrites form, which penetrate the cell separator and shorten the cell. Although the risk of dendrite formation cannot be completely ignored in lithium-ion or lithium-alloy cells, especially during high-rate charging, the risk is strongly reduced compared to lithium metal cells.

Another problem associated with the liquid electrolytes traditionally applied is leakage of the electrolyte. The leakage may not only lead to cell failure; penetration of the corrosive fluid may destroy the electronic device in which the cell is used.

One approach to solve these problems has been the application of solid state electrolytes. The use of such electrolytes will merely eliminate the risk of dendrite formation and of electrolyte leakage.

US 5,296,318 to Bell Communication Research describes the use of a polymer electrolyte based on polyvinylidene fluoride-hexafluoropropylene copolymer, which is present in the electrolyte phase in an amount corresponding to 30-80% by weight of the electrolyte system. Electrochemical cells based on such polymer electrolyte has significantly lower conductivity than cells based on a liquid electrolyte.

US 5,418,091 to Bell Communication Research describes a multistep process for the application of polymer electrolytes as described in the above US 5,296,318.

The above patents mirror the problem of solid state electrolytes, and in particular of polymer electrolytes, which are the best ambient temperature candidates; their conductivity is too low. Due to the low conductivity of the polymer electrolytes, the performance of the electrochemical cells in which they are applied is strongly reduced compared to liquid electrolyte cells.

Therefore, there is a strong need for polymer electrolytes and process technology therefor, which will provide electrochemical cells of high performance and safety, and which can be applied by a simple, low cost process.

It is thus an objective of the present invention to provide such polymer electrolytes, which display performance similar to liquid electrolytes, however, with improved safety, and processes therefor, which are simpler than traditional processing of polymer electrolytes

The objective is accomplished by a polymer electrolyte, which has a significantly lower polymer content than traditional polymer electrolytes, and which can be processed according to a simple temperature scheme.

Surprisingly it has been found, that a range of polymer electrolytes based on fluorocarbons exists, which upon heating to a certain dissolution temperature T_{dissol} produce low viscosity solutions. Such solutions are stable between room temperature and the above T_{dissol} . When additionally heated to a gelling temperature T_{gel} , $T_{\text{gel}} > T_{\text{dissol}}$, they undergo a transition, in that they upon cooling form gels of significantly higher viscosity than for the above solutions.

As used herein, a gel is defined as a system of which the modulus of elasticity is higher than the modulus of loss, i.e. it has dominating elastic properties over viscous properties

5

Such processing scheme is applied to polymer electrolytes of a polymer content in the range of 1-12% by weight of the electrolyte system. The electrolytes are then easily processable in that they are treated as liquid electrolytes until the final process step, during which the gelling takes place.

10

Thus, according to the present invention an electrolyte precursor comprising one or more solvents, one or more salts and a polymer processing the above features is heated to a temperature sufficient for the dissolution of the polymer in the solvent(s). The temperature, T_{dissol} , however, should not exceed the temperature, at which gelling of the polymer takes place upon subsequent cooling. Subsequently, the electrolyte precursor solution is incorporated into the electrochemical cell at a temperature in the range from room temperature to T_{dissol} . Following incorporation, the electrochemical cell is heated to a temperature T_{gel} . Upon subsequent cooling from T_{gel} to room temperature, a significant gelling of the electrolyte takes place, and the resulting polymer electrolyte has a significantly higher viscosity than the precursor.

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20

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In a preferred embodiment of the invention the polymer is a homopolymer or copolymer from the group of monomers of vinyl fluoride, vinylidene fluoride, trifluoroethylene, tetrafluoroethylene and hexafluoropropylene, preferably a copolymer of vinylidene fluoride and hexafluoropropylene,

30

more preferably a copolymer of vinylidene fluoride and hexafluoropropylene of a molar weight in the range 50,000-500,000, more preferably 100,000-300,000, and a weight ratio of vinylidene fluoride and hexafluoropropylene in the range 80:20 to 90:10.

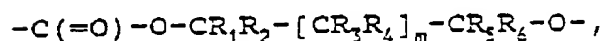
US 5,705,084 to Joseph Kejha discloses a composite solid state or semi-solid state polymer electrolyte for batteries, capacitors and other electrochemical devices, wherein the electrolyte mixture contains polyethylene oxide, polyvinylidene fluoride/hexafluoropropylene, a salt and at least one aprotic liquid. In a preferred embodiment the electrolyte comprises polyvinylidene fluoride/hexafluoropropylene in an amount in the range 0.1-70% and polyethylene oxide in an amount in the range 0.5-70% by weight of the electrolyte system, respectively. The patent discloses the coating of electrodes with solutions of the above electrolyte, prepared at 60-90°C, and the subsequent thickening of the electrolyte upon solvent evaporation. The patent, however, does not teach anything on the two stage heating and liquid phase-gel behaviour of the electrolyte, and the advantages thereof.

PCT/EP97/07275 to Danionics discloses a lithium secondary battery comprising an immobilized electrolyte containing one or more alkali metal salts, one or more non-aqueous solvents and an immobilizing polymer, wherein the immobilizing polymer is selected from the group consisting of cellulose acetates, cellulose acetate butyrates, cellulose acetate propionates, polyvinylidene fluoride-hexafluoropropylenes and polyvinylpyrrolidone-vinyl acetates with the proviso that in the case of polyvinylidene fluoride-hexafluoropropylenes, the polymer

is present in an amount of at most 12% by weight based on the weight of the salts, solvents and polymer of the electrolyte system. The patent application discloses a method for the preparation of a lithium secondary battery comprising the steps of solvent mixing, salt dissolution, addition of immobilizing polymer and sandwiching of the electrode between positive and negative electrodes. The patent, however, teaches nothing on the two stage heating scheme and the advantageous performance of the so treated electrolyte.

In a preferred embodiment of the present invention the electrolyte comprises one or more solvent(s) selected from the groups (a) to (e):

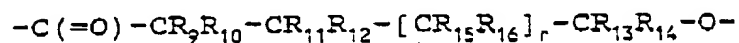
(a) alicyclic carbonates represented by the following general formula:



wherein each of R_1 , R_2 , R_3 , R_4 , R_5 and R_6 independently represents hydrogen or a C_1 - C_4 alkyl group and m is 0 or 1, preferably ethylene carbonate or propylene carbonate;

(b) aliphatic carbonates represented by the general formula $R_7[OC(O)]_pOR_8$, wherein each of R_7 and R_8 independently represents a C_1 - C_4 alkyl group, and p is an integer equal to 1 or 2, preferably dimethyl carbonate or diethyl carbonate;

(c) lactones in the form of cyclic esters represented by the general formula:



wherein each of R_9 , R_{10} , R_{11} , R_{12} , R_{13} , R_{14} , R_{15} and R_{16} independently represents hydrogen or a C_{1-2} alkyl group and r is 0 or 1, preferably γ -valerolactone or γ -butyrolactone;

5 (d) esters represented by the formula $R_{17}[C(O)]OR_{18}[OR_{19}]_t$, wherein each of R_{17} , R_{18} and R_{19} independently represents hydrogen or a C_1 - C_2 alkyl group, and t is 0 or an integer equal to 1 or 2, preferably an acetate, more preferably (2-methoxyethyl)-acetate or ethyl acetate;

10 (e) glymes represented by the general formula $R_{20}O(R_{21}O)_nR_{22}$, in which each of R_{20} and R_{22} independently represents a C_{1-2} alkyl group, R_{21} is $-(CR_{23}R_{24}CR_{25}R_{26})-$ wherein each of R_{23} , R_{24} , R_{25} and R_{26} independently represents hydrogen or a C_1 - C_4 alkyl group, and n is an integer from 2 to 6, preferably 3, R_{20} and R_{22} preferably being methyl groups, R_{23} , R_{24} , R_{25} and R_{26} preferably being hydrogen or C_1 - C_2 alkyl groups, more preferably hydrogen.

20 In a preferred embodiment of the invention the salt of the electrolyte is selected from the group of alkali metal or ammonium salts of ClO_4^- , $CF_3SO_3^-$, AsF_6^- , PF_6^- or BF_4^- , preferably $LiPF_6$ and $LiBF_4$.

25 In a preferred embodiment of the invention the electrolyte precursor comprises solvent(s), salts(s) and polymer(s) in the compositional range from 63:25:12 to 94:5:1 percent of the total weight of the electrolyte system, preferably in the compositional range from 70:20:10 to 90:8:2 percent of the total weight of the electrolyte system, more preferably
30 in the compositional range from 75:17:8 to 88:8:4 percent of the total weight of the electrolyte system.

In a preferred embodiment of the invention the dissolution temperature is in the range 45-80°C preferably 60-80°C, more preferably 65-75°C, and the gelling temperature is in the range 75-100°C, preferably 80-90°C, with the proviso, that
5 the gelling temperature should be higher than the dissolution temperature.

In a preferred embodiment of the invention the electrochemical cell comprises any one of the above
10 electrolyte configurations. The electrolyte may be confined in a separator consisting of a porous structure made of a polymer, preferably of polyethylene, polypropylene, polycarbonate or cellulose, the separator having a woven or non-woven structure having a pore size in the range of
15 10 x 10 nm to 1 x 1 mm and a thickness of 10-100µm, preferably 10-25µm. The cell further comprises a negative electrode structure comprising one or more compounds selected from the group of graphite, coke, carbon black, aluminium, silicon or tin, and a positive electrode
20 structure comprising one or more compounds selected from the group of lithium manganese oxides, lithium cobalt oxides and lithium nickel oxides.

In a further preferred embodiment the electrodes display
25 such a porosity, which allows the diffusion of a relatively solvent-rich electrolyte phase into the pores of the electrodes, leaving a relatively polymer-rich electrolyte phase in the volume between the electrodes. Such separation of the electrolyte in a pore-phase and a bulk-phase further
30 reduces the risk of electrolyte leakage. In the case of cell puncture, the low viscosity electrolyte phase will be bound in the pores and will not leak from the cell.

Similarly, the high viscosity bulk phase will be bound between the electrodes.

5 In a preferred embodiment of the invention the incorporation is applied on a wound cell, i.e. the winding of the cell is done prior to electrolyte impregnation. Such cell can be efficiently impregnated with the low viscosity electrolyte obtained from the first step of the present invention. The impregnation of wound cells further allows
10 improved control of the solvent evaporation, i.e. the solvent composition is merely unchanged during the process, even in the case of low boiling solvents such as dimethyl carbonate and diethyl carbonate.

15 In a further preferred embodiment of the invention the electrolyte incorporation is carried out by a simple pouring or injection process.

20 The invention further covers an electrochemical cell characterised by a negative electrode structure comprising one or more compounds selected from the group of graphite and coke and a positive electrode structure comprising one or more compounds selected from the group of lithium
25 manganese oxides, lithium cobalt oxides and lithium nickel oxides, preferably lithium manganese oxide, and a gelled polymer electrolyte, 1-12% by weight, preferably 4-8% by weight, of the total weight of the electrolyte being said polymer, which is selected from the group of homopolymers and copolymers from the group of monomers of vinyl
30 fluoride, vinylidene fluoride, trifluoroethylene, tetrafluoroethylene and hexafluoropropylene, preferably a copolymer of vinylidene fluoride and hexafluoropropylene.

Examples

Example 1:

5 A lithium secondary battery was prepared from a negative electrode laminate of a polymer bound carbon coated onto a copper current collector, a positive electrode laminate of a polymer bound lithium manganese oxide spinel coated onto an aluminium current collector, and an electrolyte.

10 The carbon was R-LIBA-A (product of Timcal, Switzerland). The lithium magnesium oxide spinel was prepared by a solid state reaction at 800°C from Li_2CO_3 and MnO_2 and had a specific capacity of 120 mAh/g. In the case of both
15 electrodes, the polymeric binder was EPDM (ethylene propylene diene polymethylene).

The battery laminate was wound from the above negative and positive electrode laminates and a microporous polyethylene separator. The entire battery laminate was placed in
20 plastic-coated aluminium "coffee-bag" container.

The electrolyte was prepared by mixing ethylene carbonate (EC) and diethyl carbonate (DEC) in a volume ratio of 2:1, adding LiBF_4 and LiPF_6 (60% to 40% by mole) to obtain a 1M
25 solution of $\text{LiBF}_4/\text{LiPF}_6$ in EC/DEC, heating the above liquid electrolyte solution to 70°C, and adding at this temperature 5% by weight of polyvinylidene fluoride-hexafluoropropylene (PVDF/HFP) (KYNERFLEX 2822 from Elf Atochem) to the
30 solution to obtain a 5% by weight solution of PVDF/HFP in 1M $\text{LiBF}_4/\text{LiPF}_6$ in EC/DEC. The polymer electrolyte was stirred at 70°C for ten min. before cooling to room temperature.

During these last stages, in the temperature range RT-70°C, the polymer electrolyte is in its liquid state.

5 The liquid polymer electrolyte was injected into the above battery laminate at ambient temperature. Subsequently, the battery was heated to 85°C for ten minutes. The battery was allowed to cool to room temperature.

10 At this stage, the polymer electrolyte was gelled, displaying in the bulk phase between the electrodes a viscosity significantly higher than observed for the free polymer electrolyte.

15 The battery prepared had an active electrode area of 365 cm² and, subsequent to charging to 4.2V, an internal impedance of 49 mΩ at 1kHz. When cycled between 4.2V and 2.5V at 500 mA, the battery displayed an initial capacity of 358 mAh. After 400 cycles, the capacity was 299 mAh, say 84% of the initial capacity. At 1.25A discharge rate, an initial
20 capacity of 210 mAh was observed.

Upon nail penetration (Ø=5mm, F=6000N) the battery short-circuited, however, no leakage of electrolyte was observed on the surface of the battery upon visual inspection.
25

Comparative Example 1a:

30 A battery laminate was produced and packed according to example 1. A liquid state polymer electrolyte was prepared according to example 1.

The liquid polymer electrolyte was injected into the above battery laminate at room temperature. Compared to example 1, the battery was not heated subsequent to the electrolyte injection.

5

The battery having the same dimensional characteristics as the battery of example 1, had an internal impedance of 42 mΩ at 1kHz. When cycled between 4.2V and 2.5V at 500 mA, the battery displayed an initial capacity of 408 mAh. After 400 cycles, the capacity was 343 mAh, say 84% of the initial capacity. At 1.25A discharge rate, an initial capacity of 280 mAh was observed.

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Upon nail penetration ($\phi=5\text{mm}$, $F=6000\text{N}$) the battery short-circuited. Leakage of electrolyte was observed on the surface of the battery upon visual inspection.

15

Comparative example 1b:

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A battery laminate was produced and packed according to example 1.

25

The electrolyte was prepared by mixing ethylene carbonate (EC) and diethyl carbonate (DEC) in a volume ratio of 2:1, adding LiBF_4 and LiPF_6 (60% to 40% by mole) to obtain a 1M solution of $\text{LiBF}_4/\text{LiPF}_6$ in EC/DEC, and adding at room temperature 5% by weight of polyvinylidene fluoride-hexafluoropropylene (PVDF/HFP) (KYNERFLEX 2822 from Elf Atochem) to the solution to obtain a 5% by weight solution of PVDF/HFP in 1M $\text{LiBF}_4/\text{LiPF}_6$ in EC/DEC. The polymer electrolyte was stirred at room temperature for 10 min.

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during which a partial dissolution of the polymer was observed.

5 The polymer electrolyte was injected into the above battery laminate at ambient temperature. It was observed, that the distribution of electrolyte within the battery laminate was poorer compared to the above examples 1 and 1a, as undissolved polymer was blocking the pores. Subsequently, the battery was heated to 85°C for ten minutes. The battery was allowed to cool to room temperature. The polymer electrolyte was gelled, displaying in the bulk phase between the electrodes a viscosity significantly higher than observed for the free polymer electrolyte.

15 The battery having the same dimensional characteristics as the batteries of examples 1 and 1a had an internal impedance of 150 mΩ at 1kHz. When cycled between 4.2V and 2.5V at 500 mA, the battery displayed an initial capacity of 280 mAh. After 100 cycles, the capacity was 176 mAh, say 63% of the initial capacity. At 1.25A discharge rate, 20 an initial capacity of 138 mAh was observed.

25 Upon nail penetration ($\varnothing=5\text{mm}$, $F=6000\text{N}$) the battery short-circuited, however, no leakage of electrolyte was observed on the surface of the battery upon visual inspection.

Comparative example 1c:

30 A battery laminate was produced and packed according to example 1.

The electrolyte was prepared by mixing ethylene carbonate (EC) and diethyl carbonate (DEC) in a volume ratio of 2:1, adding LiBF_4 and LiPF_6 (60% to 40% by mole) to obtain a 1M solution of $\text{LiBF}_4/\text{LiPF}_6$ in EC/DEC.

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The electrolyte was injected into the above battery laminate at ambient temperature. No gelling of the electrolyte was observed.

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The battery having the same dimensional characteristics as the battery of example 1, had an internal impedance of 38 m Ω at 1kHz. When cycled between 4.2V and 2.5V at 500 mA, the battery displayed an initial capacity of 421 mAh. After 400 cycles, the capacity was 362 mAh, say 86% of the initial capacity. At 1.25A discharge rate, an initial capacity of 360 mAh was observed.

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Upon nail penetration ($\phi=5\text{mm}$, $F=6000\text{N}$) the battery short-circuited. Leakage of electrolyte was observed on the surface of the battery upon visual inspection.

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Claims:

1. A method for the preparation of a polymer electrolyte electrochemical cell using an electrolyte precursor, said precursor comprising one or more solvents, one or more salts and a polymer which dissolves in the solvent at a first temperature (T_{dissol}) and which is capable of forming a gel on subsequent cooling following heating to a second temperature (T_{gel}), T_{dissol} being lower than T_{gel} , which method comprises:

- (a) heating the electrolyte precursor to T_{dissol} ;
- (b) optionally cooling the electrolyte precursor;
- (c) incorporating the electrolyte precursor into the electrochemical cell;
- (d) heating the electrochemical cell to T_{gel} ;
- (e) cooling the polymer electrochemical cell to ambient temperature to bring about gelling of the polymer electrolyte

2. A method for the preparation of an electrochemical cell according to claim 1, in which said polymer is a homopolymer or copolymer from the group of monomers of vinyl fluoride, vinylidene fluoride, trifluoroethylene, tetrafluoroethylene and hexafluoropropylene.

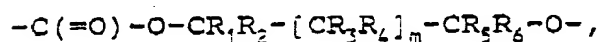
3. A method for the preparation of an electrochemical cell according to claim 2, in which said polymer is a

copolymer of vinylidene fluoride and hexafluoropropylene.

4. A method for the preparation of an electrochemical cell according to claim 3, in which said copolymer of vinylidene fluoride and hexafluoropropylene has a molar weight in the range 50.000-500.000, more preferably 100.000-300.000, and a weight ratio of vinylidene fluoride and hexafluoropropylene in the range 80:20 to 90:10.

5. A method for the preparation of an electrochemical cell according to any of the preceding claims, in which the electrolyte comprises one or more solvent(s) selected from the groups (a) to (e):

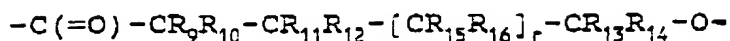
(a) alicyclic carbonates represented by the following general formula:



wherein each of R_1 , R_2 , R_3 , R_4 , R_5 and R_6 independently represents hydrogen or a C_1 - C_4 alkyl group and m is 0 or 1, preferably ethylene carbonate or propylene carbonate;

(b) aliphatic carbonates represented by the general formula $R_7[OC(O)]_pOR_8$, wherein each of R_7 and R_8 independently represents a C_1 - C_4 alkyl group, and p is an integer equal to 1 or 2, preferably dimethyl carbonate or diethyl carbonate;

(c) lactones in the form of cyclic esters represented by the general formula:



wherein each of R_9 , R_{10} , R_{11} , R_{12} , R_{13} , R_{14} , R_{15} and R_{16} independently represents hydrogen or a C_{1-2} alkyl group and r is 0 or 1, preferably γ -valerolactone and/or γ -butyrolactone;

(d) esters represented by the formula $R_{17}[C(O)]OR_{18}[OR_{19}]_t$, wherein each of R_{17} , R_{18} and R_{19} independently represents hydrogen or a C_1-C_2 alkyl group, and t is 0 or an integer equal to 1 or 2, preferably an acetate, more preferably (2-methoxyethyl)-acetate or ethyl acetate;

(e) glymes represented by the general formula $R_{20}O(R_{21}O)_nR_{22}$, in which each of R_{20} and R_{22} independently represents a C_{1-2} alkyl group, R_{21} is $-(CR_{23}R_{24}CR_{25}R_{26})-$ wherein each of R_{23} , R_{24} , R_{25} and R_{26} independently represents hydrogen or a C_1-C_4 alkyl groups, and n is an integer from 2 to 6, preferably 3, R_{20} and R_{22} preferably being methyl groups, R_{23} , R_{24} , R_{25} and R_{26} preferably being hydrogen or C_1-C_2 alkyl groups, more preferably hydrogen.

6. A method for the preparation of an electrochemical cell according to any of the preceding claims, in which the electrolyte comprises one or more salts selected from the group of alkali metal or ammonium salts of ClO_4^- , $CF_3SO_3^-$, AsF_6^- , PF_6^- or BF_4^- , preferably $LiPF_6$ and $LiBF_4$.

7. A method for the preparation of an electrochemical cell according to any of the preceding claims, in which the electrolyte comprises solvent(s), salts(s) and polymer(s) in the compositional range from 63:25:12 to 94:5:1 percent of the total weight of the electrolyte system, preferably in the compositional range from 70:20:10 to 90:8:2 percent of the total weight of the electrolyte system, more preferably in the compositional range from 75:17:8 to 88:8:4 percent of the total weight of the electrolyte system.
8. A method for the preparation of an electrochemical cell according to any of the preceding claims in which the electrolyte is confined in a separator consisting of a porous structure made of a polymer, preferably of polyethylene, polypropylene, polycarbonate or cellulose.
9. A method for the preparation of an electrochemical cell according to claim 8, in which the separator has a woven or non-woven structure having a pore size in the range of 10 x 10 nm to 1 x 1 mm.
10. A method for the preparation of an electrochemical cell according to claim 8 or 9, in which the separator has a thickness of 10-100µm, preferably 10-25µm.
11. A method for the preparation of an electrochemical cell according to any of the preceding claims, in which the electrochemical cell has a negative electrode structure comprising one or more compounds selected from the group of graphite, coke, carbon black, aluminium, silicon or tin, preferably graphite,

coke and carbon black, more preferably graphite, and a positive electrode structure comprising one or more compounds selected from the group of lithium manganese oxides, lithium cobalt oxides and lithium nickel oxides, preferably lithium manganese oxides, more preferably lithium manganese oxide LiMn_2O_4 of spinel structure.

12. A method for the preparation of an electrochemical cell according to any of the preceding claims, in which the dissolution temperature T_{dissol} is in the range $45-80^\circ\text{C}$, preferably $60-80^\circ\text{C}$, more preferably $65-75^\circ\text{C}$, and the gelling temperature T_{gel} is in the range $75-100^\circ\text{C}$, preferably $80-90^\circ\text{C}$, with the proviso, that T_{gel} should be higher than T_{dissol} .
13. A method for the preparation of an electrochemical cell according to any of the preceding claims, in which the electrochemical cell is wound prior to electrolyte impregnation.
14. A method for the preparation of an electrochemical cell according to any of the preceding claims, in which the electrolyte incorporation is carried out by pouring or injection.
15. A method for the preparation of an electrochemical cell according to any of the preceding claims, in which the electrodes of the electrochemical cell display such a porosity, that it allows for the diffusion into the pores of the electrodes of a relatively solvent-rich electrolyte phase, leaving a

relatively polymer-rich electrolyte phase in the volume between the electrodes.

16. An electrochemical cell characterised by a negative electrode structure comprising one or more compounds selected from the group of graphite and coke and a positive electrode structure comprising one or more compounds selected from the group of lithium manganese oxides, lithium cobalt oxides and lithium nickel oxides, preferably lithium manganese oxide, and a gelled polymer electrolyte, 1-12% by weight, preferably 4-8% by weight, of the total weight of the electrolyte being said polymer, which is selected from the group of homopolymers and copolymers from the group of monomers of vinyl fluoride, vinylidene fluoride, trifluoroethylene, tetrafluoroethylene and hexafluoropropylene, preferably a copolymer of vinylidene fluoride and hexafluoropropylene.

Abstract**Polymer Electrolyte Electrochemical Cell**

5 The invention relates to a method for the preparation of
a polymer electrolyte electrochemical cell using an
electrolyte precursor, said precursor comprising one or
more solvents, one or more salts and a polymer which
dissolves in the solvent at a first temperature (T_{dissol})
and which is capable of forming a gel on subsequent
10 cooling following heating to a second temperature (T_{gel}),
 T_{dissol} being lower than T_{gel} , which method comprises:

- (a) heating the electrolyte precursor to T_{dissol} ;
- 15 (b) optionally cooling the electrolyte precursor;
- (c) incorporating the electrolyte precursor into the
electrochemical cell;
- 20 (d) heating the electrochemical cell to T_{gel}
- (e) cooling the polymer electrochemical cell to
ambient temperature to bring about gelling of the
polymer electrolyte

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Preferably the polymer is a homopolymer or copolymer from
the group of monomers of vinyl fluoride,
vinylidenefluoride, trifluoroethylene, tetrafluoroethylene
and hexafluoropropylene.

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